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SUBJECT: Problem Statement - Treatment of Declad Wastes for Disposal

TO: F. L. Culler

FROM: J. T. Roberts and W. E. Tomlin

ABSTRACT

It is proposed that decladding wastes be converted to dry solid "packages" suitable for ultimate storage in a dry environment. Low temperature solidification of Sulfex and Zirflex decladding wastes by addition of lime, plaster of paris, portland cement, drying agents, etc. seems feasible. A similar treatment of Darex decladding wastes probably should be preceded by chloride removal and nitrate destruction. Calcination may be a preferable alternative for Darex wastes.

1.0 INTRODUCTION

Chemical decladding of stainless-steel-clad and zirconium-clad reactor fuel elements by the Sulfex, Darex and Zirflex processes produces large volumes of high-chemical-concentration, intermediate-radiochemical-level wastes (Table 1). A study has shown that for permanent disposal of power reactor wastes in tanks, the decladding wastes contribute more to the total cost than the associated high-level solvent extraction waste concentrates.[2] The present Chemical Technology Division waste treatment program is based on the philosophy that permanent tank storage is not acceptable as an "ultimate" solution to the nuclear waste disposal problem, for reasons of safety more than economics.

Table 1. Compositions and Volumes* of Decladding Wastes[1]

Sulfex	Darex	Zirflex
4.4 M H^+	2.7 M H^+	0.75 M NH_4^+
3.3 M SO_4^{-2}	1.5 M Cl^-	1.5 M F^-
1.0 M SS	3.6 M NO_3^-	0.2 M Zr^{+4}
	0.83 M SS	0.02 M NO_3^-
		0.003 M Sn^{+4}
		0.0075 M Al^{+3}
2140 gals/ton**	2560 gals/ton**	4200 gals/ton***

*Volumes are expressed as gallons per metric ton (1000 kg) of uranium-plus-thorium.

**The Sulfex and Darex waste volumes were calculated for Consolidated Edison reactor fuel.

***The Zirflex waste volume was calculated for PWR blanket fuel.

The present development program is aimed at converting the high-level wastes to thermally-stable dry solids by calcination in a stainless-steel pot, which will also serve as the waste container during "ultimate" storage in a dry environment such as a concrete vault, limestone cave or salt mine. Because of the "defense in depth" inherent in the storage of low-mobility solids in high-integrity containers in a dry environment, "non-leachability" is not considered to be a controlling factor.

It is proposed that part of the chemical technology program be aimed at developing treatment methods for decladding wastes which are consistent with the philosophy adopted for high-level waste treatment.

2.0 SUMMARY

It is proposed that decladding wastes be converted to dry solid "packages" suitable for ultimate storage in a dry environment. Because the total radioactivity of the decladding wastes is only about 0.1% of that of the high level wastes, the self-heating of the stored wastes by the energy of radioactive decay is much less of a problem than with the high level wastes. Thus it should be acceptable to solidify the decladding wastes at lower temperatures and in larger packages than is proposed for the high level wastes. The lower temperature preparation is desirable since the high-temperature calcination of sulfate-, chloride- and fluoride-bearing wastes involves severe corrosion and off-gas problems in comparison with calcination of nitrates. Working with larger packages is desirable in that this minimizes the total number of packages to be handled, an important consideration since the decladding wastes have large volumes compared to the high-level wastes, and also minimizes container cost since larger containers have lower surface-to-volume ratio.

A one-man laboratory effort along these lines is planned for the present, with unit operations effort added when laboratory developments warrant. First priority will be given to the solidification of Sulfex decladding waste by adding lime to form a "gypsum." Solidification of Zirflex decladding waste is given second priority. One possibility for accomplishing this is to add lime, to precipitate the fluoride and zirconium, plus calcium sulfate or portland cement, to cause the mixture to set up. Lowest priority will be given to Darex decladding waste, because the calcination of high-level Darex wastes is being studied and this treatment could also be used on the decladding waste (after chloride removal), and because a straight-forward method of preparing a low-temperature, low-solubility solid is not readily apparent.

3.0 SULFEX DECLADDING WASTE

Lime neutralization of Sulfex decladding waste was demonstrated by Flanary and Goode[3] in 1957. They showed that the "gypsum" formed contained the iron-chromium-nickel and most of the fission products in relatively insoluble form, with cesium being the main source of activity in aqueous leach liquors.

Recent scouting studies have been more concerned with the physical integrity of the solid block formed and indications are that the quality of the block depends critically on the method of preparation. When dry CaO or $Ca(OH)_2$ powder is added to Sulfex decladding waste there is considerable evolution of heat and unless this is dissipated the mixture heats itself to the boiling point and evolves steam. The evolution of steam can cause the resultant solid to have voids in it, increasing its volume and decreasing its strength. The temperature to which the mixture is heated also affects the setting rate and the quality of the solid formed. The stainless-steel hydroxides present also apparently affect the quality of the block deleteriously, tending to give "damp" rather than "dry" cakes. Addition of the lime as an aqueous slurry alleviates the heating problem somewhat and makes it easier to mix the reactants uniformly, by giving a thinner "paste" which stirs easier, but is "borderline" as far as cake quality is concerned since gypsym will not set if too much water is added and the water-to-sulfate ratio in Sulfex decladding waste is already fairly high. It may be necessary to add plaster of paris ($CaSO_4 \cdot 1/2H_2O$) or portland cement or a water absorbent in order to get a hard, strong, dry cake.

It is planned to study cake "quality" i.e.,

volume and density,
strength,
setting-up time,
thermal conductivity,
heat of reaction,
leachability,
vapor pressure and off-gassing,
etc.

as a function of such preparation variables as concentration of reactants, order of addition, temperature of reaction, subsequent temperature history, etc.

4.0 ZIRFLEX DECLADDING WASTE

Recent scouting studies have shown that addition of lime to Zirflex decladding waste precipitates the fluoride and the zirconium but the resulting slurry does not set up to a hard cake. Presumably a cake could be prepared by adding calcium sulfate, portland cement, calcium silicate cement, etc. It is proposed to conduct more scouting experiments along this line at the present time, with a priority lower than Sulfex but higher than Darex decladding waste studies.

When this waste is made alkaline some ammonia is given off and it may be desirable to deliberately drive it all off to prevent subsequent off-gassing in storage. It would be possible to drive the fluoride off too by acidifying and heating, producing a Sulfex-like waste if sulfuric acid were used. This would involve a corrosion problem and would generate another fluoride waste unless the recovered fluoride could be recycled. Calcination is another possibility, but would also involve a severe corrosion problem.

It might be possible to mix Zirflex and Sulfex decladding wastes together and then solidify by adding lime. Mixing the two wastes in a processing plant may not be practical, however.

5.0 DAREX DECLADDING WASTE

While the Darex decladding waste undoubtedly could be solidified by adding enough calcium sulfate or cement, the resulting block would have a high content of water-soluble nitrate and chloride salts. While a high degree of insolubility is not felt to be a necessary criterion for the storage of solid wastes in a dry environment, a Darex "concrete" block would be inferior to similar Sulfex and Zirflex blocks in this respect. Chloride removal from Darex decladding waste could be accomplished by distillation in the standard Darex feed-adjustment manner. Most of the nitrate could be removed by treatment with NO, as shown by Savolainen,[4] or HCHO. The resulting stainless-steel-hydroxide slurry could then be solidified.

This solidification approach is being assigned a priority below Sulfex and Zirflex at present since the current high-level calcination is applicable to Darex decladding wastes, after chloride removal, but probably not to the other two.

6.0 MANPOWER

Present plans are that W. E. Tomlin will spend ~ 80% of his time on this problem until enough information is obtained to warrant either an increase in effort or a shift in direction. (The balance of his time will be spent on thermochemical studies of waste components, at present primarily coordination with E. and M. and Instruments in getting new equipment built and installed.)

7.0 REFERENCES

1. F. R. Bruce, "The Origin and Nature of Radioactive Wastes in the Atomic Energy Program," ORNL-CF-59-11-6.

2. W. G. Stockdale, E. D. Arnold, J. O. Blomeke, "Economics of Permanent Disposal of Power Reactor Wastes in Tanks," (in press), ORNL-2873.

3. J. R. Flanary and J. H. Goode, "Chemical Technology Division Monthly Progress Reports," June-October (1957), ORNL Nos. 2362, 2385, 2400, 2416, and 2417.

4. J. E. Savolainen, "Chemical Technology Division Monthly Progress Report for Chemical Development Section B, May 1959," ORNL-CF-59-6-64.

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